Crystal and geometry-optimized structure, Hirshfeld surface analysis and spectroscopic studies of tetrachlorocuprate and nitrate salts of 1-(2-fluorophenyl)piperazine cations, (C₁₀H₁₅FN₂)[CuCl₄] (I) and (C₁₀H₁₄FN₂)[NO₃] (II)

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Abstract

Two new organic-inorganic hybrid materials, 1-(2-fluorophenyl)piperazine-1,4-dium tetrachlorocuprate, (C₁₀H₁₅FN₂)[CuCl₄] (**I**) and 1-(2-fluorophenyl)piperazin-4-ium nitrate, (C₁₀H₁₄FN₂)[NO₃] (**II**), have been synthesized by an acid/base reaction at room temperature in the presence of 1-(2-fluorophenyl)piperazine as an organic-structure directing agent and their structures were determined by single crystal X-ray diffraction. Compound (**I**), (C₁₀H₁₅FN₂)[CuCl₄], crystallizes in the monoclinic system and *P*2₁/*c* space group with *a* = 7.5253 (2), *b* = 20.6070 (7), *c* = 9.7281 (3) Å, *β* = 103.6730 (17)°, *V* = 1465.82 (8) Å³ with *Z* = 4. Full-matrix least-squares refinement converged at *R* = 0.037 and *wR*(*F*²) = 0.088. Compound

(II), (C₁₀H₁₄FN₂)[NO₃], belongs to the monoclinic system, space group *P*2₁/*c* with the following parameters: *a* = 10.8034 (2), *b* = 7.5775 (1), *c* = 14.4670 (3) Å, β = 111.761 (2)°, *V* = 1099.91 (4) Å³ and *Z* = 4. The structure was refined to *R* = 0.044, *wR*(*F*²) = 0.136.

In the structures of **(I)** and **(II)**, the anionic and cationic entities are interconnected by means of set of hydrogen bonding contacts forming three-dimensional networks. Intermolecular interactions were investigated by Hirshfeld surfaces and the contacts of the four different chloride atoms were notably compared. The results of the optimized molecular structure are presented and compared with the experimental one. The Molecular Electrostatic Potential (MEP) maps and the HOMO and LUMO energy gap of both compounds were computed. The vibrational absorption bands were identified by infrared spectroscopy. Theory (DFT) calculations of normal mode frequencies are compared with experimental ones.

Keywords: X-ray diffraction; Hirshfeld surface; hybrid compounds; IR; NMR; DFT.

In the last few years, organic-inorganic hybrid materials have drawn much attention as new generation of high performance materials by reason of their interesting chemical and physical properties obtained from the combination of organic and inorganic materials in a single compound and device application due to their optical, electronic, efficient luminescence, magnetic properties, plastic mechanical properties and hence multifunctional behavior [1 - 12]. Among solid-state physicists and chemists, there is a great interest in copper(II) halides owing to the plasticity of the metal coordination sphere which leads a great variety of crystalline architectures with different coordination numbers, geometries and nuclearities, and makes copper(II) systems excellent candidates for analyzing correlations between structural parameters and magnetic properties [13 - 16].

Another aspect that makes especially copper(II) complexes quite interesting is that many complexes have been found to have the potential for treatment of cancers and other diseases

[17] and these complexes have drawn great attention for their high nucleolytic efficiency [18 - 27]. The transition metal complexes, especially copper(II) complexes, are known to be effective against rheumatoid arthritis and they also show anti-ulcer activity [28, 29].

The halocuprates and their properties are of interest not only in inorganic chemistry but also in fields ranging from solid-state physics to bioinorganic chemistry. Their diversity and ability to easily interconvert into each other makes these systems excellent candidates for analyzing correlations between structural parameters, magnetic and optical properties [30, 31].

On the other hand, coordination chemistry of oxanions does not cease developing and is the subject of main research topic in several laboratories. Oxanions, such as sulfates, phosphates, molybdates, nitrates, perchlorates, selenites, iodates, etc., are Lewis bases used as ligands for elaborate interesting metal complexes having applications in various fields: stabilization of PVC, protection of wood, catalysis, pesticides, fungicides, pharmacology etc... [32 - 36]. Several works were focused on copper(II) halides to study the influence of the organic cation features on the packing interactions that govern the structural organization and consequently on the properties of this kind of complex [37, 38].

Some organic cations (protonated amines) can be used as stabilizing of these anions especially those that are acidic [39 - 41]. The piperazine and its derivatives, for example, have interesting pharmacological, cardiovascular and autonomic properties such as a high affinity for the dopamine D₂ receptor and/or the serotonin reuptake site, and the ability to treat conditions related to disturbances in the dopaminergic and/or the serotonergic systems such as anxiety disorders, depression, Parkinson's disease, and schizophrenia [42 - 44].

Since the synthesis of low molecular weight copper(II) complexes and related ligands, their structural characterization, the analysis of their coordination modes and intermolecular interaction are important to better understand structure-property relationships, and in view of

our continued involvement in the investigation of halocuprates and nitrate compounds [45, 46], we report here the synthesis, crystal structures and IR characterization of two new tetrachlorocuprate and nitrate salts of 1-(2-fluorophenyl)piperazine cation, $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ (**I**) and $(\text{C}_{10}\text{H}_{14}\text{FN}_2)[\text{NO}_3]$ (**II**).

The organic-inorganic hybrid compound, $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ (**I**), was prepared by reaction of 1-(2-fluorophenyl)piperazine, $(\text{C}_{10}\text{H}_{13}\text{FN}_2)$ and copper chloride. First, CuCl_2 (1 mmol; 0.17 g) was added to a 1-(2-fluorophenyl)piperazine (1 mmol; 0.19 g) solution in 15 mL of absolute ethanol. The resulting solution was then acidified with 1 mL of concentrated HCl and allowed to evaporate slowly at room temperature. Brown plate like crystals of $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ were formed after two weeks (yield, 87.7 %). Elem. anal., Calc.: C, 30.96; H, 3.87; N, 7.22%. Found: C, 30.78; H, 3.67; N, 7.39%.

Compound (**II**) was synthesized from an aqueous mixture of 1-(2-fluorophenyl)piperazine, $(\text{C}_{10}\text{H}_{13}\text{FN}_2)$ and nitric acid 65% (1 mmol) with a stoichiometric ratio of 1:1 at room temperature followed by slow evaporation at room temperature over several days leading to formation of transparent crystals (yield 91.1 %). Elem. anal., Calc.: C, 49.33; H, 5.75; N, 17.26%. Found: C, 49.54; H, 5.52; N, 17.66%. More experimental details are given in supplementary information.

Single crystals of (**I**) and (**II**) were carefully selected under a microscope and mounted on a Mitegen micromesh with the help of a trace of mineral oil. For (**I**), X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Intensities were corrected for Lorentz polarization and absorption effects [47]. The structure was solved by direct methods with the *SIR97* suite of programs [48] and refinements were performed on F^2 by full-matrix least-squares methods with all non-hydrogen atoms anisotropic using *SHELXL2014/7* [49]. The N-H hydrogen atoms were found in the difference Fourier map

and refined isotropically; all other hydrogens were included on calculated positions, riding on their carrier atoms. The intensity data of **(II)** were collected on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector using the same MoK α radiation. Crystal was cooled at 110 K by a low temperature nitrogen blower. Diffraction frames were processed with *CrysAlisPRO* program [50]. First structure model solution was found with *ShelXT* program [51] and model refinement was done with *SHELXL2014/7* [49]. CIF file was completed with Olex2 [52]. For both **(I)** and **(II)** crystals, $\omega/2\theta$ scan technique was used to collect the diffraction frames.

The drawings were made with Diamond [53]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

The NMR spectra were recorded on solid-state high-resolution Bruker Avance-300 spectrometer operating at 75.48 MHz for ^{13}C and Avance-500 operating at 470.38 MHz for ^{19}F with a classical 4 mm probe head allowing spinning rates up to 10 kHz. ^{13}C and ^{19}F NMR chemical shifts are given relative to tetramethylsilane and fluorotrichloromethane, respectively (precision 0.5 ppm). The carbon spectrum was recorded by use of cross polarization (CP) from protons (contact time 2 ms) and magic angle spinning (MAS). Before recording each spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the protons (typically 100 s). For fluorine a direct excitation was used with a recycle delay of 100 s.

Fourier Transform Infrared (FTIR) spectra of powder samples were obtained by use of a Nicolet 5700 spectrophotometer from potassium bromide (KBr) pellets (2 mg of sample in 200 mg of KBr). The number of scans was 32. The scanning range was 4000 - 400 cm^{-1} and the resolution 2 cm^{-1} .

The NMR chemical shifts and infrared spectrum were calculated with the Gaussian 09 software. The calculations were made by use of the B3LYP method. The basis set was 6-311++G** for all atoms. The positions of the atoms were those determined by the X-ray diffraction study except for the hydrogen atoms which were first optimized at the above level of theory. The chemical shifts were then calculated by use of the GIAO method.

The unit formula of the title compound, (C₁₀H₁₅FN₂)[CuCl₄] (**I**), is made up of one inorganic tetrachlorocuprate(II) anion and one 1-(2-fluorophenyl)piperazine-1,4-dium dication (Fig. 1). The copper atom is bounded to four chlorine atoms, giving a distorted tetrahedral geometry coordination of *D*_{2d} symmetry. The distortion from the ideal tetrahedron can be ascribed to the Jahn Teller effect, that is reflected in the present compound by the value of the trans Cl-Cu-Cl angles, of 123.69(2) and 134.01(2)° [54] (Table 2), as well as by the observed orange color [55]. The Cl-Cu-Cl angles can be analyzed though the τ_4 metric developed by Yang [56]. The τ_4 value is calculated from: $\frac{[360 - (\alpha + \beta)]}{141}$, where α and β are the two largest angles. A value of zero (0) is indicative of an ideal square-planar geometry while a value of one (1) indicates an ideal tetrahedral geometry. The calculated τ_4 value of the title compound is $\tau_4(\text{Cu}) = 0.725$, indicating a small distortion from a regular tetrahedron. The shortest Cu...Cu distances are 6.336(2) and 7.316(0) Å, the intramolecular Cl...Cl distances are between 3.408(0) and 4.099(3) Å.

In the packing arrangement, the anions and cations are interconnected via N-H...Cl hydrogen bonds, forming a *R*₂⁴(12) motif, to give tetrameric aggregates located at (0,0,0) and (0,½,½) (Fig. 2a and Table 4a). The phenyl rings of the cationic molecules connect these moieties through C-H...Cl and N-H...Cl hydrogen bonds and form layers parallel to the (**a**, **c**) plane and situated around $y = n/2$ (Figs. 2b, 2c).

A CSD search of N-phenylpiperazinium dication salts resulted in 15 hits. In the majority of cases the anion is of MCl_4^{2-} type, where M is a metal; in particular, three structures contain tetrachlorocuprate ions, i.e. NIKQUV [57], OGINUP [58] and PHPIPZ [59]. The $\tau_4(\text{Cu})$ value for these three complexes has been calculated to be 0.60, 0.51 and 0.54 for NIKQUV, OGINUP and PHPIPZ, respectively, indicating a distortion from a regular tetrahedron geometry slightly higher than the one observed in **(I)**. On the other hand, all the CuCl_4^{2-} structures show a similar N-H...Cl interactions pattern (Table 4a), irrespective of the different phenylpiperazinium substituents, where only three Cl atoms are involved, and with N...Cl distances varying in the range 3.088 - 3.293 Å. The dissimilarities in CuCl_4^{2-} geometry deformation seem, then, to be ascribable to other intermolecular interactions, e.g. C-H...Cl contacts.

The asymmetric part of the unit cell of compound **(II)** contains one 1-(2-fluorophenyl)piperazin-4-ium cation and one NO_3^- anion as shown in Fig. 3. The atomic arrangement can be described by ribbons of inorganic entities, made up from NO_3^- anions and NH_2^+ groups, developed parallel to the *b*-axis direction at $z = 1/4$ and $z = 3/4$ (Fig. 4a). The organic groups are inserted between these ribbons and connect them via C-H...O hydrogen bonds (Fig. 4b). In this material, the monoprotonated 1-(2-fluorophenyl)piperazine cations are linked to the nitrate anions by multiple bifurcated and trifurcated N-H...O and weak C-H...O hydrogen bonds, forming a three-dimensional network, with donor-acceptor distances varying between 2.802(2) and 3.582(2) Å (Fig. 4b, Table 4b). Interatomic bond lengths and angles of the nitrate anions spread respectively within the ranges 1.2368(7) - 1.2776(7) Å and 118.75(5) - 121.93(5)°. These geometrical features have also been noticed in other related crystal structures [45]. It is worth noting that the recently published N-pyrimidinylpiperazinium nitrate salt [60] is isostructural with **(II)**, presenting the same space group and very similar unit cell parameters and hydrogen bonding pattern (Fig. 4c).

As in **(II)**, the interactions governing the packing arrangement are those between the nitrate ion and the NH₂ group; neither the fluorine atom of the fluorophenyl moiety nor the nitrogen atoms of the pyrimidine substituent are involved in intermolecular interactions, although weak, indicating that the observed supramolecular synthons can be reproducible.

As for the organic cations, the phenyl rings in **(I)** and **(II)** exhibit a regular spatial configuration with normal C-C distances and C-C-C, angles (Tables 2 and 3). The C-C bond lengths vary from 1.369(3) to 1.400(1) Å which are between a single and double bond and agree with those in the literature [57]. For the piperazine-1,4-dium ring, the C-N and C-C bond lengths are in the range 1.461 to 1.518 Å. These values, which clearly indicate single bonds, agree well with those observed in other similar compounds [61].

The conformation of the piperazine six-membered ring can be described in terms of Cremer and Pople puckering coordinates [62], i.e., evaluating the parameters Q (total puckering amplitude), q_2 , q_3 , θ and φ . The calculated values are as follows: $Q = 0.5894$ Å, $q_2 = 0.0321$ Å, $q_3 = 0.5885$ Å, $\theta = 3.12^\circ$ and $\varphi = 18.93^\circ$ for compound **(I)** and $Q = 0.5802$ Å, $q_2 = 0.0668$ Å, $q_3 = 0.5764$ Å, $\theta = 6.61^\circ$ and $\varphi = -9.80^\circ$ for compound **(II)**, which correspond in both cases to the structure of the most stable chair conformation.

A comparison between the title compounds: 1-(2-fluorophenyl)piperazine-1,4-dium tetrachlorocuprate(II) **(I)** and 1-(2-fluorophenyl)piperazin-4-ium nitrate **(II)**, shows that the two compounds differ only by the nature of the inorganic anions. This situation affects the unit cell parameters but not the space group. In fact, both compounds crystallize in the same $P2_1/c$ space group of the monoclinic system ($Z = 4$). In addition, the geometrical parameters of the organic groups are comparable and are similar to those observed in other complexes containing the same cations. However, in both compounds the NH₂⁺ ions connect the inorganic entities, via

N-H...Cl hydrogen bonds in **(I)** to form dimers and through N-H...O hydrogen bonds in **(II)** to form ribbons.

The optimized gas phase structures of both compounds (C₁₀H₁₅FN₂)[CuCl₄] (**I**) and (C₁₀H₁₄FN₂)[NO₃] (**II**) were determined using DFT/B3LYP method with the LANL2DZ basis set. The selected calculated structural parameters of both compounds are listed in Tables 2 and 3 with XRD data. The results of the optimized molecular structure are presented and compared with the experimental ones. In compound **(I)**, the bond lengths of Cu1-Cl4 = 2.24380 Å, Cu1-Cl2 = 2.27209 Å and Cu1-Cl3 = 2.33747 Å are larger than the experimental values of Cu1-Cl4 = 2.2052(6) Å, Cu1-Cl2 = 2.2596(5) Å and Cu1-Cl3 = 2.2937(5) Å. The Cu1-Cl1 bond distance calculated 2.235111 Å by B3LYP is just 0.0127 Å lower than the reported experimental value of 2.2478 Å. Slight variations in the rest of bond lengths and angles are observed such as Cl1-Cu1-Cl2, Cl2-Cu1-Cl3, N2-C2-C1, C5-C10, C8-C9, N2-C2, C5-N1-C4, N2-C3-C4 and C3-N2-C2. In **(II)**, the experimental N-O bond lengths and O-N-O angles vary between 1.2368(7) and 1.2776(7) Å and 118.75(5) - 121.93(5)°, respectively, while these geometrical parameters are computed at the interval 1.22554 - 1.26588 Å and 117.90339 - 122.62952°, respectively.

In the organic cation in compound **(II)**, the bond angles show a good agreement between the experimental and theoretical values. The discrepancies between these geometrical parameters arises from the calculation method used. Indeed, the experimental results belong to solid phase of molecules, while the calculation results apply to the gas phase of an isolated molecule without any intermolecular interactions with neighboring molecules in the crystal packing.

The fingerprint plot of contacts on the Hirshfeld surface was generated using Crystal Explorer [63]. The two dimensional fingerprint plots generated represent the exterior and inner (d_e and d_i) distances and are shown for the two major contacts H...Cl and H...C (Fig. S1). The analysis contacts enrichment on the Hirshfeld surface was carried out using the MoProViewer

[64] software. The nature of the intermolecular contacts in the crystal structure is shown in Table 5. The enrichment ratios [65] of contacts between the different chemical species were computed in order to highlight which interactions are over-represented with respect to equiprobable contacts computed from the surface composition. The Hirshfeld surface was computed around the independent organic cation and one CuCl_4 anion (Fig. S2).

The organic cation surface is covered by 72% of hydrogen (Hc and Hn); Hc and Hn represent the hydrogen atoms bound to carbon and nitrogen, respectively. Globally the Hc and Cl^- chemical types constitute the largest proportions (36.1 and 34.8%) of the Hirshfeld surface on the cation and anion present the asymmetric unit. Consequently, the $\text{Hc}\dots\text{Cl}^-$ weak hydrogen bonds represent the largest interaction surface at 40.6% (Table 5) and their occurrence is slightly enriched at $E = 1.6$. The Hn hydrogen atoms have a larger partial charge and have the ability to form strong hydrogen bonds with the chloride atoms, and the $\text{Hn}\dots\text{Cl}$ contacts are indeed the most enriched ($E = 2.6$). There are three $\text{N-H}\dots\text{Cl}^-$ hydrogen bonds in the crystal structure and all three Hn atoms interact exclusively with the CuCl_4 anions.

Hydrophobic contacts involving C, Hc and F atoms between organic cations represent only 20% of the contact surface. Chloride and hydrogen atoms constitute together more than three quarters of the total Hirshfeld surface; as a consequence after formation of the CuCl_4 anion, the crystal packing is essentially maintained by the attractive and enriched strong $\text{Hn}\dots\text{Cl}^-$ and weak $\text{Hc}\dots\text{Cl}^-$ hydrogen bonds.

The Hirshfeld surface analysis was used to describe the chemical nature of the intermolecular interactions in the crystal structure of compound **(II)** (Fig. S3). Analysis of the Hirshfeld surface of the organic cation in the structure mapped with d_{norm} function reveals several red areas indicating close contacts between the organic molecules and the nitrate anions (Fig. S3a). The red areas correspond to hydrogen bonds formed between protonated nitrogen

atoms of the organic moieties and the oxygen atoms of the nitrate ions. The smaller red spots correspond to weaker C-H...O interactions connecting the organic molecule and the nitrate ion.

It is found that O...H contacts are the dominant intermolecular interactions at 36% due to the abundance of oxygen and hydrogen on the molecular surface (above 21 and 52%, respectively) (Fig. S4). In compound (**II**), the O...Hc contacts show enrichment ratios around 1.24 and constitute the most frequent interaction type as the relative contribution reaches one quarter (Table 6). The O...Hn contacts are the most enriched at $E_{\text{OHn}} = 3.8$ and indicate the strongly enhanced presence of ionic interactions between the organic cations and the nitrate anions.

However Hc...C and Hc...F constitute 22.1 and 7.7% of the Hirshfeld surface and are over-represented ($E_{\text{HcC}} = 1.39$, $E_{\text{HcF}} = 1.68$). Hc...Hc contacts constitute as much as 15% of contacts but are the only hydrophobic interaction which is under-represented. The percentage of C...C (4.3%) interactions is not negligible and shows a slight over-representation with an enrichment ratio of 0.95 and indicates the presence of π - π interactions between fluorophenyl rings in this crystal structure. This suggests that van der Waals forces play also an important role in the crystal packing of compound (**II**). The Hc...F contacts are enriched in accordance to a previous study [55] indicating that hydrogen is a preferred partner in contacts made by organic F atoms, as the two atom types are weakly charged and are attractive from an electrostatic point of view.

The molecular electrostatic potential of the compound (**I**) has been computed at the B3LYP/6-31+G* level and is shown in Fig. 5a. The molecular electrostatic potential (MEP) is used to predict the molecular reactive behavior towards electrophilic and nucleophilic attack and defined sites of the electrophile and nucleophile. The different values of the MEP at the surface are represented by different colors. The red regions represented the most electronegative

electrostatic potential. The blue regions represented the most positive electrostatic potential and green regions relieve that the potential is zero. As seen from Fig. 5a, the MEP is calculated around the anion and cation separately. The negative charge covers the CuCl_4^{2-} anion that can be considered as nucleophilic while the organic cation has the reactive electrophile sites; these sites are involved in mutual intermolecular contacts [66]. The molecular electrostatic potential (MEP) surfaces of compound **(II)** were also computed at the B3LYP/6-31+G* level of theory by Gaussian 09 software [67]. As seen from Fig. 5b, the MEP surface of the compound **(II)** was calculated also for the anion and the cation separately. That is evident that the negative charge is around the N=O group of the nitrate anion and the potential energy is positive over the N-H group of the organic cation. According to these results, we can say that there is a global electrostatic attraction between the organic cation and inorganic anion.

HOMO-LUMO orbitals were calculated from the crystal Data with B3LYP/6-31+G* for both Compounds **(I)** and **(II)**. In compound **(I)**, the HOMO/LUMO calculations were made separately for the tetrachlorocuprate(II) anion and of the organic cation. The HOMO and LUMO orbitals on the tetrachlorocuprate(II) have an energy of 1.033 and 3.887 eV respectively. In the organic cation, the HOMO orbital is concentrated on the aromatic ring and the LUMO orbital is located mainly on one nitrogen atom of the NH_2 group. The energy gap between the HOMO and LUMO is 5.443 eV which characterizes a good stability for the organic ligand (Fig. S5a). On the other hand, we cannot know the stabilization of this complex since they are two different entities with completely different energy levels (positive values for the copper complex and negative for the organic ligand). In compound **(II)** and as seen from Fig. S5b, the highest occupied orbitals are localized on the part of the aromatic ring and the nitrogen atom of the piperazine ring, while the lowest unoccupied orbitals are located primarily on the other nitrogen atom of piperazine ligand. The HOMO-LUMO gaps of 4.39 eV for compound **(II)** implies high kinetic stability and low chemical reactivity [68, 69], because it is energetically

unfavorable to add electron to a high-lying LUMO or to extract electrons from a low-lying HOMO [70]. This large HOMO-LUMO gap means is of great importance for potential applications in chemical catalysis, electro-optic [71], conductor [72], and other applications [73].

Since the compound **(I)** is paramagnetic, only the compound **(II)** was studied by multinuclear solid state (^{13}C and ^{19}F) MAS-NMR. ^{19}F MAS-NMR spectrum of crystalline $(\text{C}_{10}\text{H}_{14}\text{FN}_2)[\text{NO}_3]$ **(II)** is given in Fig. S6. It exhibits only one peak at -116.5 ppm with six corresponding satellite spinning side bands. The existence of a single peak indicates the presence of only one fluorine crystallographic site in the unit cell, which agrees with the X-ray results.

The ^{13}C CP-MAS NMR spectrum of **(II)** is shown in Fig. S7. It exhibits in the aliphatic carbon resonance region, only one broad and asymmetric peak at 43 ppm. The resonance of the four carbon atoms of the piperazinic ring are in close proximity with substantial overlap. This is also in agreement with one molecule being present in the asymmetric unit cell as revealed by X-ray structure determination. In the aromatic carbon resonance region, six lines are observed in agreement with the presence of only phenyl ring in the unit cell of **(II)** as revealed by X-ray results.

In order to confirm the above attributions, theoretical calculations were undertaken. The absolute chemical shifts were calculated by using the GIAO method. These calculated values were then calibrated relative to tetramethylsilane with $\delta_{\text{exp}} = 0$ ppm. The carbon atoms are labeled as depicted Scheme I:

Scheme I. Atom labels.

The results are listed on Table 7. Clearly, there is a very good agreement between the experimental and theoretical values calculated after optimization of the positions of the protons, confirming the above attribution of the NMR signals.

To gain information on the crystal structure, we have carried out a vibrational study using infrared absorption. The infrared spectra of both compounds recorded at room temperature are shown in Fig. S8. Based on some studies carried out for previous works and reported on similar nitrate and perchlorate compounds [74], we propose an attempt of assignment of the observed bands.

The molecular structures of both compounds have various functional groups such as NH_2^+ , NH^+ , C-H, C-N, C=C and disubstituted benzene ring. These groups are expected to undergo changes in their intensity and position according to their environments [75].

Hydrogen bonding interactions are able to affect the frequency as well as the intensity and width of these vibrations. As these structures feature N-H...O hydrogen bonds, the N-H stretching modes are altered largely. In the high-frequency region, the observed bands between 3400 and 3100 cm^{-1} correspond to the stretching vibrations of the NH_2 and N-H groups, while those in the range 3000 - 2700 cm^{-1} are assigned to the C-H stretching mode [76]. The comparison between the IR spectra of the two salts (**I**) and (**II**) with that of the pure amine (Fig. S8) shows that the widths of these bands are more significant in the salts which is attributed to

the formation of hydrogen bonds N-H...Cl and C-H...Cl in **(I)** and N-H...O and C-H...O in **(II)**. It should be noted that the widths of the bands are greater in **(II)** because its network of hydrogen bonds network is significantly richer (Tables 4 (a & b)). The band at about 1620 cm⁻¹ is attributed to the NH₂ in-plane deformation mode. The two bands at 1580 and 1500 cm⁻¹ correspond to the C=C aromatic stretching modes. The bands between 1450 and 1300 cm⁻¹ are assigned to CH₂ deformation modes. The intense bands at about 1250 and 1150 cm⁻¹ were assigned to C-N stretching. The observed band at about 1030 cm⁻¹ was attributed to asymmetric and symmetric C-C stretching modes. The observed band at 760 cm⁻¹ is assigned to C-H out-of-plane deformation, while that at 620 cm⁻¹ corresponds to (C-N-C) and (C-C-N) deformation vibrations.

For the NO₃⁻ anion, Fig. S8 shows different groups of bands between 1400 and 700 cm⁻¹. In this case, the intense peak appears at 1328 cm⁻¹ shows the presence of asymmetric stretching vibration of NO₃⁻ (ν_3). The bands between 1150 - 930 cm⁻¹ are related to the symmetric stretching modes $\nu(\text{NO}_3^-)$. Then, we attribute the observed weak bands at 810 cm⁻¹ and 721 cm⁻¹ respectively to the $\gamma(\text{NO}_3^-)$ out of the plane and $\delta(\text{NO}_3^-)$ in the plane bending modes.

DFT calculations of the frequencies were made on the geometry obtained after optimization of the protons. An additional calculation was also made on the anion and the contributions of the two components were summed to lead the full spectrum. The resulting IR spectra between 500 and 4000 cm⁻¹ are shown on Fig. S9 (a & b) for **(I)** and **(II)**, respectively, and are very similar to the experimental ones. A close agreement between the experimental and theoretical wavenumbers is mostly achieved in the finger print region as shown in Fig. S10. Thus, the precision is well-sufficient to assign the experimental frequencies and to confirm the attributions proposed above.

Both compounds, $(C_{10}H_{15}FN_2)[CuCl_4]$ (**I**) and $(C_{10}H_{14}FN_2)[NO_3]$ (**II**), are characterized by single crystal X-ray diffraction, Hirshfeld surface analysis, DFT and FT-IR spectroscopy. According to our X-ray structural results, the structure of compound (**I**) consists of organic cations which are linked to the inorganic anions via N-H...Cl hydrogen bonds to form dimers and via N-H...O to form ribbons in the structure of compound (**II**). Hirshfeld surface analysis shows different types of intermolecular interactions including hydrogen bonding. The MEP map shows that the negative potential sites are on electronegative inorganic part as well as the positive potential sites are around the organic cation in both compounds (**I**) and (**II**). The HOMO-LUMO energy gaps suggest a good stability of both compounds. DFT vibrational analysis of both compounds allows a reliable assignment of the organic cation and show good agreement between calculated and experimental wavenumbers.

Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1537238 for (**I**) and 1538229 for (**II**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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Fig. 1 View of the asymmetric unit in the crystal structure of $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ (**I**) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

- (a) **Fig. 2** View along the a -axis showing $\text{N-H}\cdots\text{Cl}$ hydrogen bonds in (**I**) forming kind of 12-membered rings.
- (b) Projection of the atomic arrangement of $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ (**I**) structure along the c -axis. Hydrogen bonds are shown as dashed lines.
- (c) Projection in the (a, c) plane of a layer situated at $y = 0$ in the crystal structure of $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ (**I**). The dotted lines indicate hydrogen bonds.

Fig. 3 View of the contents of the asymmetric unit of **(II)**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 4

- (a) View of ribbons of inorganic entities in **(II)**, made up from NO₃⁻ anions and NH₂⁺ groups along *a*-axis.
- (b) Packing diagram of **(II)**, viewed down the *b*-axis. Hydrogen bonds are shown as dashed lines. Generic labels show the atom types.
- (c) Hydrogen bonding pattern around the cation in N-pyrimidinylpiperazinium nitrate.

(a)

(b)

Fig. 5 Molecular Electrostatic Potential map of the two compounds **(I)** (a) and **(II)** (b).

Table 1 Crystal data and structure refinement parameters of (C₁₀H₁₅FN₂)[CuCl₄] and (C₁₀H₁₄FN₂)[NO₃].

Formula	(C ₁₀ H ₁₅ FN ₂)[CuCl ₄]	(C ₁₀ H ₁₄ FN ₂)[NO ₃]
Formula weight (g.mol ⁻¹)	387.58	243.24
Crystal system / Space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	295	110 (1)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.5253 (2), 20.6070 (7), 9.7281 (3)	10.8034 (2), 7.5775 (1), 14.4670 (3)
<i>β</i> (°)	103.6730 (17)	111.761 (2)
<i>V</i> (Å ³)	1465.82 (8)	1099.91 (4)
<i>Z</i>	4	4
<i>μ</i> (Mo <i>Kα</i>) (mm ⁻¹)	2.21	0.121
Crystal size (mm)	0.53 × 0.21 × 0.06	0.43 × 0.26 × 0.07
Diffractometer	Nonius Kappa CCD diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan	Gaussian
<i>T</i> _{min} , <i>T</i> _{max}	0.412, 0.617	0.524, 1.000
No. of measured, independent and observed [<i>I</i> > 2.0 σ(<i>I</i>)] reflections	14524, 4261, 3302	74976, 9252, 6612
<i>R</i> _{int}	0.065	0.041
(sin θ/λ) _{max} (Å ⁻¹)	0.704	1.003
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.088, 1.03	0.044, 0.136, 1.07
No. of reflections	4261	9252
No. of parameters	175	154
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.59, -0.82	0.62, -0.36

Table 2 Main interatomic distances (Å) and angles (°) of (C₁₀H₁₅FN₂)[CuCl₄] (**I**).

Parameters	XRD Data	Theoretical data
Inorganic anion		
Cu1-Cl4	2.2052(6)	2.24380
Cu1-Cl2	2.2596(5)	2.27209
Cu1-Cl1	2.2478(5)	2.23511
Cu1-Cl3	2.2937(5)	2.33747
Cl4-Cu1-Cl1	134.01(2)	132.84664
Cl1-Cu1-Cl2	102.23(2)	105.56866
Cl1-Cu1-Cl3	99.97(2)	101.38485
Cl4-Cu1-Cl2	101.74(2)	102.77499
Cl4-Cu1-Cl3	98.46(2)	98.89740
Cl2-Cu1-Cl3	123.69(2)	121.83201
Organic cation		
N1-C5	1.479(2)	1.48176
N1-C1	1.512(2)	1.52687
N2-C2	1.484(3)	1.52297
C1-C2	1.513(3)	1.52911
C5-C10	1.369(3)	1.40596
C6-C7	1.378(3)	1.39390
C8-C9	1.372(3)	1.40703
N1-C4	1.506(2)	1.51557
N2-C3	1.488(2)	1.52053
F1-C6	1.351(2)	1.39452
C3-C4	1.518(3)	1.53102
C5-C6	1.384(2)	1.40696
C7-C8	1.379(3)	1.40676
C9-C10	1.392(3)	1.40718
C5-N1-C4	111.91(14)	114.40603
C4-N1-C1	108.94(14)	108.48308
N1-C1-C2	109.83(16)	110.46295
N2-C3-C4	110.64(17)	113.44038
C10-C5-C6	119.76(18)	118.21739
C6-C5-N1	116.65(17)	118.35048
F1-C6-C5	117.78(16)	118.48465
C6-C7-C8	118.12(19)	118.55126
C8-C9-C10	120.9(2)	120.48392
C5-N1-C1	113.64(15)	112.78135
C3-N2-C2	111.49(14)	114.71323
N2-C2-C1	110.47(16)	113.33191
N1-C4-C3	110.35(15)	110.26034
C10-C5-N1	123.56(16)	123.39446
F1-C6-C7	120.47(17)	118.86135
C7-C6-C5	121.7(2)	122.65007
C9-C8-C7	120.7(2)	120.01054
C5-C10-C9	118.9(2)	120.08644

Table 3 Main interatomic distances (Å) and angles (°) of (C₁₀H₁₄FN₂)[NO₃] (**II**).

Parameters	XRD Data	Theoretical data
Inorganic anion		
O3-N3	1.2776 (7)	1.26588
O2-N3	1.2425 (7)	1.22554
O1-N3	1.2368 (7)	1.25446
O2-N3-O3	118.75 (5)	122.62952
O1-N3-O3	119.31 (5)	117.90339
O1-N3-O2	121.93 (5)	119.46708
Organic cation		
F1-C1	1.3558 (7)	1.36440
N1-C6	1.4093 (6)	1.41713
N1-C7	1.4651 (7)	1.47155
N1-C10	1.4611 (7)	1.46132
N2-C9	1.4952 (8)	1.48971
N2-C8	1.4939 (7)	1.49063
C5-C6	1.3987 (7)	1.40561
C5-C4	1.3944 (8)	1.39834
C6-C1	1.4005 (7)	1.40647
C1-C2	1.3797 (8)	1.38478
C7-C8	1.5153 (8)	1.52510
C2-C3	1.3956 (10)	1.39864
C10-C9	1.5179 (8)	1.52722
C4-C3	1.3897 (10)	1.39488
C6-N1-C7	116.93 (4)	116.09456
C6-N1-C10	116.88 (4)	117.11540
C10-N1-C7	110.36 (4)	111.49003
C8-N2-C9	112.14 (4)	112.83905
C4-C5-C6	121.21 (5)	121.37638
C5-C6-N1	123.88 (5)	123.75543
C5-C6-C1	116.32 (5)	116.30151
C1-C6-N1	119.61 (5)	119.89990
F1-C1-C6	118.28 (5)	118.58611
F1-C1-C2	118.16 (5)	118.11777
C2-C1-C6	123.52 (5)	123.29246
N1-C7-C8	109.79 (4)	110.16035
C1-C2-C3	118.90 (6)	119.11579
N1-C10-C9	108.72 (4)	109.78013
N2-C9-C10	110.78 (5)	109.70485
N2-C8-C7	110.61 (4)	109.49612
C3-C4-C5	120.67 (5)	120.48167
C4-C3-C2	119.33 (5)	119.42260

Table 4 Bond length (Å) and angles (°) in the hydrogen bonding scheme of (C₁₀H₁₅FN₂)[CuCl₄] **(I) (a)** and (C₁₀H₁₄FN₂)[NO₃] **(II) (b)**.

(a)

D-H...A	D-H	H...A	D...A	D-H...A
N2-H3N...Cl1 ⁱ	0.87	2.65	3.314(1)	134
N2-H2N...Cl2 ⁱⁱⁱ	0.94	2.16	3.088(2)	166
C3-H3B...Cl2 ⁱⁱ	0.97	2.85	3.703(1)	147
N1-H1N...Cl3	0.85	2.41	3.260(3)	170

Symmetry codes: (i) $-x-1, -y, -z+1$; (ii) $-x, -y, -z+1$; (iii) $x, y, z+1$.

(b)

D-H...A	D-H	H...A	D...A	D-H...A
N2-H2A...O2 ^v	0.89	2.88	3.452(0)	124
N2-H2A...O2 ⁱⁱ	0.89	2.58	3.034(2)	112
N2-H2A...O3 ⁱⁱ	0.89	1.99	2.846(2)	161
N2-H2B...O1	0.89	2.67	3.445(0)	146
N2-H2B...O3	0.89	1.95	2.802(1)	160
C2-H2...O3 ^{iv}	0.93	2.82	3.582(2)	140
C3-H3...O1 ⁱ	0.93	2.56	3.352(4)	143
C9-H9B...O1 ⁱⁱⁱ	0.97	2.56	3.400(1)	144
C9-H9B...O2 ⁱⁱⁱ	0.97	2.75	3.366(2)	122
C10-H10A...O1	0.97	2.60	3.461(1)	147

Symmetry codes: (i) $-x+1, y-1/2, -z+1/2$; (ii) $-x+2, y-1/2, -z+3/2$ (iii) $-x+2, -y+1, -z+1$; (iv) $x-1, -y+1/2, z-1/2$; (v) $x, y-1, z$.

Table 5 Chemical proportions on the Hirshfeld surface of the organic cation and CuCl_4^{2-} anion in (**I**). (Hc and Hn represent the hydrogen atoms bound to carbon and nitrogen, respectively). N atoms represent 0.5% of the surface and omitted). Actual contact types and their enrichment in the crystal packing of the title compound are also given. The major contacts and the most enriched are highlighted in bold.

Atom	Hn	C	F	Cl	Cu	Hc
%	6.9	12.8	3.5	34.8	5.7	36.1
Hn	0.0					
C	0.0	1.5		contacts	(%)	
F	0.0	0.4	0.2			
Cl	12.4	10.1	2.3	2.4		
Cu	0.9	1.1	0.9	1.4	0.0	
Hc	0.0	10.6	3.0	40.6	7.4	4.4
Hn	0.0					
C	0.0	1.0		enrichment		
F	0.0	0.5	1.7			
Cl	2.6	1.1	0.9	0.2		
Cu	1.2	0.7	2.2	0.3	0.0	
Hc	0.0	1.2	1.2	1.6	1.8	0.4

Table 6 Chemical proportions on the Hirshfeld surface, the interactions and their enrichments of the $(\text{C}_{10}\text{H}_{14}\text{FN}_2)[\text{NO}_3]$ compound. The major contacts are highlighted in bold.

Atom	Hn	C	N	O	F	Hc
%	6.6	17.7	3.2	21.1	5	46.3
Hn	0.0					
C	0.1	4.3				
N	0.0	0.8	0.0			
O	11.1	2.6	0.2	1.8		
F	0.0	0.0	0.5	0.8	0.4	
Hc	2.3	22.1	4.6	24.9	7.7	15.8
Hn	0.00					
C	0.06	1.46				
N	0.09	0.80	0.00			
O	3.80	0.35	0.12	0.39		
F	0.00	0.02	1.70	0.38	1.66	
Hc	0.36	1.39	1.61	1.24	1.68	0.73

Table 7 Comparison of calculated and experimental chemical shift values of the carbon atoms in **(II)**.

Atoms	δ_{th} (ppm)	δ_{exp} (ppm)
C1	48.3	broad signal at 43 ppm
C2	50.2	
C3	47.3	
C4	47.2	
C5	127.7	137.1
C6	151.7	152.0 and 155.5 ($^1J_{C-F} = 265$ Hz)
C7	114.1	116.7
C8	123.6	122.3
C9	120.7	
C10	111.7	113.8

Supplementary Information

Fig. S1

2D Fingerprint plot of the main interactions (reciprocal interactions are merged). (a) H...Cl: 62%, (b) H...C: 9%.

(a)

(b)

Fig. S2

Hirshfeld surface around the organic cation and CuCl_4 anion. The colors are according to the interior (a) and exterior (b) atom contributing most to the electron density.

Fig. S3

Hirshfeld surface of **(II)** mapped with d_{norm} function. (a) Around the cation $\text{C}_{10}\text{H}_{14}\text{N}_2\text{F}$. (b) Around the nitrate anion.

Fig. S4

Decomposed two dimensional fingerprint plots for the Hirshfeld surface around the organic molecule and the anion in the compound **(II)** crystal. The major intermolecular interactions are shown.

Fig. S5

Frontier molecular orbitals (HOMO and LUMO). (a) Compound **(I)**. (b) Compound **(II)**.

Fig. S6

^{19}F MAS NMR spectrum of **(II)**. * Spinning sidebands.

Fig. S7 ^{13}C CP-MAS NMR spectrum of (II).

Fig. S8 Experimental IR spectrum of the two compounds (I) and (II) and the pure amine.

Fig. S9

Calculated IR spectrum. (a) $(\text{C}_{10}\text{H}_{15}\text{FN}_2)[\text{CuCl}_4]$ (**I**). (b) of $(\text{C}_{10}\text{H}_{14}\text{FN}_2)[\text{NO}_3]$ (**II**).

(a)

(b)

Fig. S10

Comparison between experimental and calculated IR frequencies. (a) $(C_{10}H_{15}FN_2)[CuCl_4]$ (I) and (b) $(C_{10}H_{14}FN_2)[NO_3]$ (II).